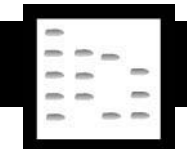
CHROMATOGRAPHY: GAS



Column Technology

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Introduction

It is the role of the column to achieve separation of the components of injected mixtures. In many cases, it is also possible to accomplish *extra-column* 'separation', i.e. 'separation' by distinguishing between merged or co-eluting solutes. Selective detectors, such as the flame photometric detector, are useful in this regard, but our focus here will be directed toward separation as accomplished in the column.

The resolution equation is usually presented in one of two popular forms:

$$N_{req} = 16R_s^2[(k+1)/k]^2[\alpha/(\alpha-1)]^2 \quad [1]$$

or:

$$R_s = 1/4\sqrt{N}[k/(k+1)][(\alpha-1)/\alpha] \quad [2]$$

Equation [1] is used to estimate the number of theoretical plates that will be required (N_{req}) to separate any two solutes to some specified degree of resolution (R_s), as functions of the retention factor (k) of the second of those two solutes, and of their separation factor (α). These relationships will be utilized later.

Equation [2] emphasizes that resolution (i.e. the degree to which solutes are separated) is affected by only three parameters: (1) the number of theoretical plates (N); (2) solute retention factors (k); and (3) solute separation factors (α).

The number of theoretical plates is a function of the 'sharpness' of a peak, relative to the time that the solute spends in the column. The measurement is affected by the length of the solute band introduced into the column (it is assumed that this is infinitesimally small, which is never the case), the length (L) and radius (r_c) of the column, the retention factor (k) of the solute, and the average linear velocity ($\bar{u}$) of the carrier gas. It can also be affected by the thickness of the stationary phase film (d_f), and by solute diffusivity in the stationary phase (D_S). Small values of k yield disproportionately large values of N. This anomaly essentially disappears with values of $k \geq 5$.

The parameters affecting the solute retention factor (k) can be deduced from the inviolable relationship that must always exist between k, the distribution constant (K_c), and the column phase ratio (β):

$$K_c = \beta k \quad [3]$$

From this, it is evident that $k = K_c \times 1/\beta$, or (using the definitions in the Glossary):

$$k = c_S/c_M \times V_S/V_M \quad [4]$$

For a given solute, k varies directly with solubility of that solute in the stationary phase (e.g. the k value of pentane would, under similar conditions, be higher in a polydimethylsiloxane stationary phase than in a polyethylene glycol stationary phase). In a given stationary phase, k varies indirectly with temperature: as the temperature increases, c_S decreases and c_M increases, and k decreases in a manner that is essentially exponential.

Finally (as evidenced in eqns [3] and [4]), k varies inversely with the column phase ratio, β (or directly with $1/\beta$). In other words, solute retention factors (k) increase as the volume of column occupied by stationary phase (V_S) increases and/or the volume occupied by mobile phase (V_M) decreases. In packed columns, β is usually controlled by the stationary phase 'loading'; in the open-tubular column, β is controlled primarily through d_f, and to a smaller extent, through r_c. There are some practical limitations: where $d_f < 0.1$ μm, columns can exhibit excessive activity, as evidenced by 'tailing' (reversible and irreversible adsorption) of 'active' solutes. Where $d_f > 1.0$ μm (or even less if $D_M < 10^{-7}$ cm^2 s^{-1}), the mass transport term of the van Deemter equation (C_M) becomes limiting, and column efficiency (as reflected by N) decreases. Solute retention factors interrelate with determinations of N. Unless the gas velocity is so high that solutes can no longer undergo equilibrium partitioning (this would require extremely high velocities), k is independent of $\bar{u}$.

Comparisons of Packed and Open-Tubular Columns

One thousand plates per foot of column length, or approximately 3000-plates per metre, represents the best that can be expected from a packed column; although packed columns rarely achieve this value, it is often exceeded in the open-tubular system. The

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length of the packed column is limited in practice to about 5 m, because the packing offers a much greater resistance to gas flow than does the open tube. As a result, the packed column can deliver a maximum of about 15 000 theoretical plates, which pales in comparison to the 150 000 to 500 000 theoretical plates that can be attained in the modern open-tubular columns. Some work has been reported using longer packed columns operated under extreme pressures, but these applications have not proven practical in a working environment.

In the open-tubular column, the theoretical maximum achievable efficiency can be estimated from the fact that:

$$H = L/N \qquad [5]$$

and:

$$H_{\text{theor min}} = r_c\{[(11k^2) + 6k + 1]\}^{1/2}/[3(1 + k)^2] \qquad [6]$$

It was mentioned in earlier discussions of k that small values of k exhibit disproportionately large values of N (or small values of H). If we use eqn [6] to calculate $H_{\text{theor min}}$ and $N_{\text{theor max}}$ for a 0.25 mm open-tubular column, we obtain the values shown in **Table 1**. A graph of these data (**Figure 1**) stresses the very large values of N that are obtained for small values of k. Note that this effect becomes negligible as $k \geq 5.0$.

For many years, packed columns offered a distinct advantage to the analyst concerned with the separation of highly volatile solutes, because the phase ratio (β) of the packed column is rarely greater than about 30, while the phase ratios of early wall-coated open-tubular columns were usually about 300. From eqn [3], it is evident that solute retention factors (k) will be some 10 times greater (300/30) on packed columns than on these early open-tubular columns, with all other conditions constant.

Table 1 Maximum theoretical values of the numbers of theoretical plates per metre of column length ($N\,m^{-1}$) as a function of the retention factor (k) of the test solute. Values are calculated for a 0.25 mm column, and assume $D_M = 0.6\ cm^2\ s^{-1}$ and $D_S = 10^{-7}\ cm^2\ s^{-1}$

k	N (m^{-1}), theoretical maximum
0.01	13 582
0.1	11 661
1	6 531
2.5	5 270
5	4 753
7	4 505
10	4 362

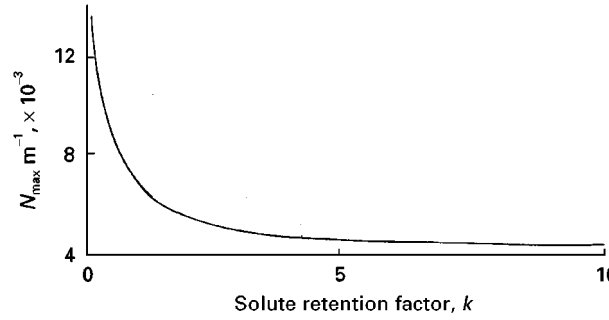

Figure 1 Graph of the data shown in Table 1, maximum theoretical values of the numbers of theoretical plates per metre of column length ($N\,m^{-1}$) as a function of the retention factor (k) of the test solute. Values are calculated for a 0.25 mm column, and assume $D_M = 0.6\ cm^2\ s^{-1}$, and $D_S = 10^{-7}\ cm^2\ s^{-1}$.

The number of theoretical plates that will be required to separate any two solutes is the product of three multipliers in eqn [1]: (1) the degree of resolution required [$16R_s^2$] (for baseline separation, $R_s \cong 1.5$, and this one multiplication factor becomes 36); a squared ratio of the separation factors $[\alpha/(\alpha - 1)]^2$, and a squared ratio of the retention factors $[(k + 1)/k]^2$. A highly volatile solute might exhibit $k = 0.01$ on one of these earlier open-tubular columns, and the $[(k + 1)/k]^2$ multiplier would therefore be $[101/1]^2 \cong 10\,000$. On the packed column, the phase ratio is lower, and the k of this solute (all other conditions constant) would increase by the factor $300/30 \times 0.01 \cong 0.1$. This results in the $[(k + 1)/k]^2$ multiplier becoming 121 instead of 10 000, and the number of theoretical plates required for the separation of this low-k solute has been decreased by two orders of magnitude.

Because of these relationships, the packed column user was more successful in attaining the separation of some highly volatile (low-k) mixtures that resisted separation on the wall-coated open-tubular columns of those times. The subsequent development of cross-linked and surface-bonded stationary phases permitted the manufacture of open-tubular columns with much thicker films of stationary phase – 3, 5 and 8 μm. In a 0.25 mm column, these give phase ratios of 20.8, 12.5 and 7.8, respectively, and this particular advantage of the packed column disappears. Alternatively, retention factors are usually significantly higher on porous-layer open-tubular (PLOT) columns that utilize the more retentive mode of gas–solid adsorption chromatography rather than gas–liquid partition chromatography. Even fixed gases such as argon, nitrogen, oxygen can be resolved on such columns.

Thick-film open-tubular columns suffer some distinct disadvantages, however. The exploration of this is facilitated by an examination of the van Deemter

equation. In its packed column form, this can be expressed as

$$H = A + B/\bar{u} + C\bar{u} \quad [7]$$

where A is the eddy diffusion or packing factor term, B is the longitudinal diffusion term and C is the resistance to mass transfer term. Because H is a function of $1/N$, the smaller the sum of these terms, the smaller H, and the more efficient the system. (Efficiency equations really represent the efficiency not of the column, but of the total system. A number of extra-column factors – the injection process, extra volume in the injector and detector, too low a split ratio or make-up gas flow, lag time in signal acquisition – detract from system efficiency, but efficiency equations attribute all of this to the column.) The open-tubular column has no packing, and the A term can be discarded to yield the Golay equation: $H = B/\bar{u} + C\bar{u}$. Some major differences between packed and open-tubular columns become more apparent if the C term is expanded to distinguish mass transfer from stationary phase to mobile phase (C_s) from mass transfer from mobile phase to stationary phase (C_M):

$$H = B/\bar{u} + \bar{u}[C_M + C_S] \quad [8]$$

In packed columns, most of the interior volume of the column is occupied by the particles of support material; each particle is covered with a relatively thick film of stationary phase, and there is a minuscule gas volume in the interstitial space between the particles. Hence the volume of stationary phase is large, the volume of mobile (gas) phase is small, and the packed column typically has a smaller phase ratio or β. In the packed column, the magnitude of the C term is largely a function of mass transfer from stationary to mobile phase (C_S). A solute molecule dissolved in stationary phase takes some time before it re-enters the mobile phase, where it must proceed only a minuscule distance through the carrier gas (C_M) before it again enters stationary phase. C_S is the *limiting factor* in the packed column, but C_M is trivial: hence, hydrogen, helium, nitrogen, argon–methane or carbon dioxide yield essentially the same efficiencies when used as the mobile phase in packed columns.

In the open-tubular column, a much thinner film of stationary phase is on the wall of a tube, which while usually of capillary dimension, requires solute molecules to traverse a much longer flow path through the mobile phase. Thus the transverse distance across the open-tubular column is significantly greater than the interparticle distance encountered in packed columns. As a consequence, column efficiency (and the optimum average linear velocity of the carrier gas) varies directly with the diffusivity of the mobile phase. In the open-tubular column, C_M is the limiting factor and C_S is trivial – until we come to the thick-film open-tubular column. In this case, *both* C_S *and* C_M are significant; the major advantage of the open tubular column has been sacrificed, and column efficiency suffers.

An analogous limitation is encountered with low diffusivity stationary phases. In the polydimethylsiloxane stationary phase, D_s for a C_{12} compound at 150°C approximates to $1 \times 10^{-7}\,cm^2\,s^{-1}$. At this value, columns yield about the same efficiencies when the stationary phase film (d_f) is varied from 0.1 to 0.4 μm; at $d_f > 0.4$ μm, the efficiencies of columns coated with this stationary phase begin to decrease. Polysiloxanes are relatively permeable, and substitutions that increase the carbon/oxygen ratio (e.g. phenyl) have an adverse effect on that permeability. This lowers the value of D_s, and column efficiency – in terms of plates per metre – decreases, unless d_f is also decreased. As an example, smaller values of d_f are desirable on columns coated with polymethylsiloxanes containing phenyl, cyanopropyl and/or polyethylene glycol-type substituents, where a significant increase in efficiency is exhibited by 0.15 μm film columns as compared to 0.25 μm films. As the rate of diffusion through the stationary phase decreases (this is a function of D_s), the distance the solute must travel through that stationary phase (a function of d_f) becomes increasingly important.

Many investigators have contributed to our progress in stationary phase and column developments. While a thorough discussion of the interrelationships and significance of these contributions is beyond the scope of this article, the Further Reading section include some of the more salient efforts in column developments.

The Stationary Phase

Many of the disparate materials employed as 'liquid phases' on the earliest packed columns soon proved unsatisfactory for open-tubular columns. It was eventually realized that higher temperature stabilities in open-tubular columns required highly viscous phases whose viscosity endured at the operating temperatures. With this realization, the polysiloxanes attracted interest, because they could be cross-linked to produce a semisolid gum-like phase; the term 'stationary phase' soon replaced 'liquid phase' in common usage. Columns coated with these materials exhibited higher temperature tolerances and longer lifetimes. This is another area in which a multitude of individual investigators have contributed to progress.

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As discussed earlier, packed columns are typically limited to lengths that can generate 10 000 to 15 000 theoretical plates because of their higher pressure drops. With this restriction on N, the separation factor, α, becomes more critical to the packed column (eqn [2]), and α is best controlled through the choice of stationary phase. While α values do respond to changes in temperature, the direction of any given response can be predicted only for solutes whose functionalities are similar. For example, in a series of methyl ketones or a series of paraffin hydrocarbons, α values vary inversely with temperature. But if the column temperature is decreased for a sample containing a mixture of methyl ketones and paraffin hydrocarbons, one can predict only that the α of any two hydrocarbons (and that of any two ketones) will increase. The α of a mixed pair – hydrocarbon and ketone – can increase or decrease as the temperature is lowered, and that effect will be reversed if the temperature is raised. In short, the effect of temperature on α cannot be predicted for two solutes of different functionality. Hence for any given group of mixed solutes, α values are controlled primarily through experience and observations on the probability of interactions between given solutes and a given stationary phase.

The limitation on N and the resultant increased reliance on α made stationary phase selectivity of major import to the packed column, and has been largely responsible for the proliferation of some 300 different stationary phases for packed columns. Because much higher numbers of theoretical plates are attainable in open-tubular columns, solute separation factors – α – were initially less critical to the user of open-tubular columns. However, the inexorable increase in the demands placed upon the analytical chemist ultimately necessitated the development of high-N columns coated with high-α phases.

Low-Bleed Columns

As the column temperature is increased, there is an increase in the steady-state baseline signal. The chemical bonds of the stationary phase are under increased thermal stress, degradation fragments are produced at an increased but constant rate, and the baseline signal rises and remains steady as long as that temperature is maintained. In polysiloxane stationary phases, the degradation fragments consist largely of cyclic siloxanes, dominated by trimers and tetramers of (–Si–O–) to which the methyl (or other) substituents occupying the remaining two bonds of the tetravalent silicon atom may remain attached, or may cleave. True column bleed does not generate peaks or humps; a signal that rises and then falls must have a 'point source'. Bleed signal is annoying with any bleed-sensitive detector, and can be the limiting factor in GC-MS, especially with the newer ion trap mass spectrometers (ITD). For a given quality of stationary phase under a given set of conditions (temperature, carrier gas flow), bleed is always a function of the mass of stationary phase in the flow path. Hence, shorter, smaller diameter, thinner film columns will exhibit lower bleed levels than longer, larger diameter, thicker film columns.

At the present time, column bleed is usually reported in terms of pA of FID (flame ionization detector) signal at a given temperature, but this is an imprecise specification. It would be better to report bleed as 'pg carbon emitted per unit time' as measured on a *calibrated* detector. Only where the same detector is used under the same conditions for both determinations can different columns be truly compared in terms of 'pA of FID signal'. Bleed signal from polysiloxane columns is generally attributed to cyclic siloxanes that usually arise from thermal and/or oxidative degradation of the phase, but contaminants in the detector or in gas lines supplying that unit, materials outgassing from septa and ferrules, and contaminating oils from column installation also contribute to what is *perceived* as column bleed. The latter sources are usually (but not always) dwarfed by the former, but their significance increases in the case of low bleed columns. It should also be noted that at elevated temperatures, even a pristine FID *without any column* generates 1–2 pA signal.

Some years prior to the invention of gas chromatography, Sveda, a Du Pont chemist working on bulk polymers, filed two patents on silarylene–siloxane polymers. Shown in **Figure 2** are generic structures of (A) the conventional 95% dimethyl–5% diphenylpolysiloxane (in which the phenyl groups are pendant to the siloxane chain), and (B) Sveda's poly(tetramethyl-1,4-silphenylene siloxane).

Not surprisingly, the two forms display somewhat different selectivities toward solutes. More than 40 years after Sveda's work, several column manufacturers began offering proprietary 'low-bleed' columns that would appear to be based on the silarylene siloxanes. The lengthy delay may have been partly due to the fact that, until quite recently, bleed rates from high quality 'conventional' columns were not considered excessive in most applications. A more probable cause is that silarylene polymers are not yet commercially available, so that those wishing to utilize them must resort to a sequential series of in-house syntheses that are both materials and labour intensive, each step of which is usually characterized by low yields.

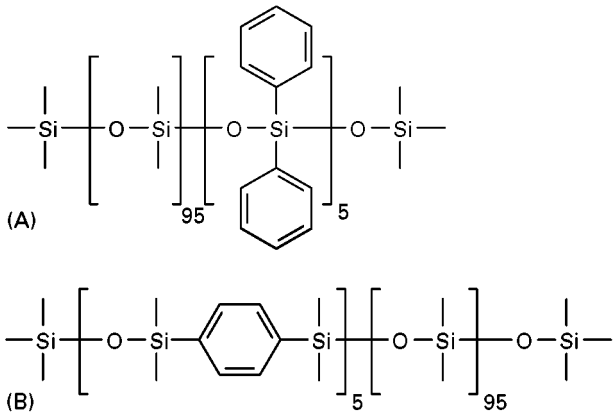

Figure 2 Generic structures of (A) the conventional 95% dimethyl – 5% diphenylsiloxane and (B) Sveda's poly (tetramethyl-1,4-silphenylene siloxane).

Several pathways have been postulated for the thermal degradation of siloxanes, some of which require a proximity of two normally separated groups that would require folding of the siloxane chain. It has been suggested that such reactions might be blocked by the insertion of groups that would make the chain more rigid and restrict its flexibility. Such efforts have led to the introduction, by more than one manufacturer, of stationary phases that are characterized by the generation of lower bleed signals, even at elevated temperatures, e.g. 360°C.

Figure 3 contrasts the bleed profiles of examples of 'first generation' (a silphenylene siloxane) and 'second generation' (a silphenylene siloxane containing 'chain-stiffening' groups) low-bleed columns. Note that the latter not only exhibits a bleed level about half that of the former, but the bleed pattern is simpler, making the phase especially valuable for those utilizing bleed-sensitive detectors such as the ion trap mass spectrometer. It also possesses a unique selectivity that has excited great interest among those interested in a variety of problematic separations, including the polychlorinated biphenyl congeners.

Column performance is also influenced by the deactivation, or surface preparation treatment. The observation that thin-film columns often exhibit adsorption toward active solutes, and that thicker films of stationary phase result in more inert columns,

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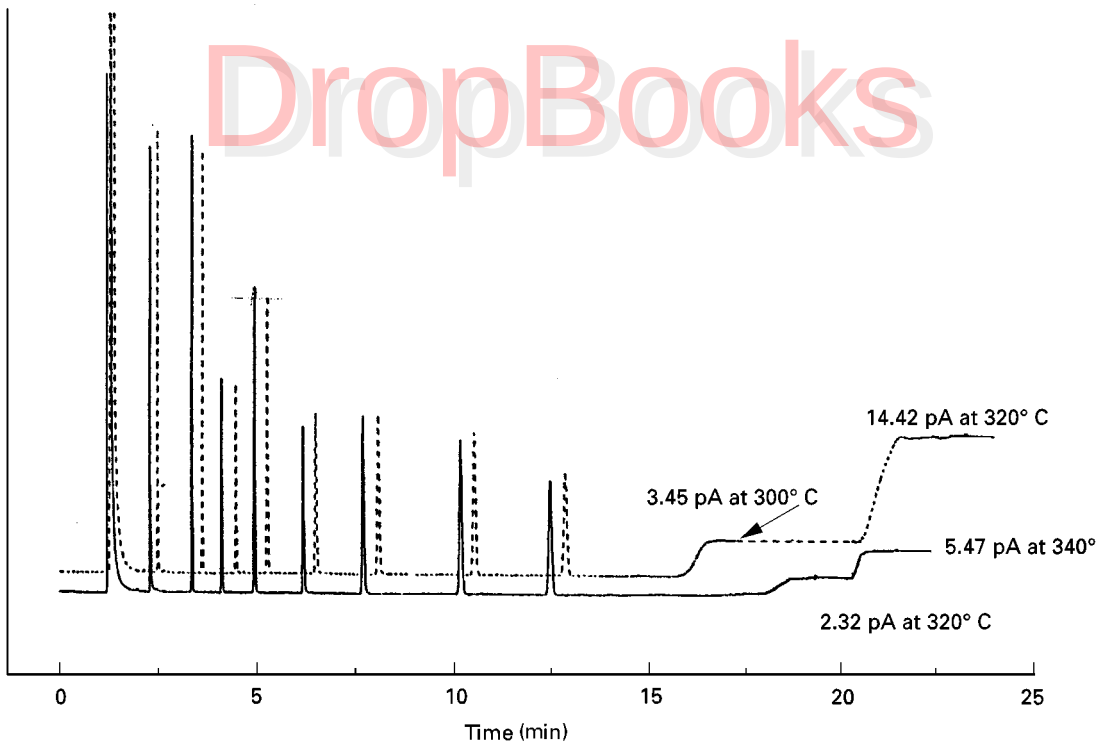
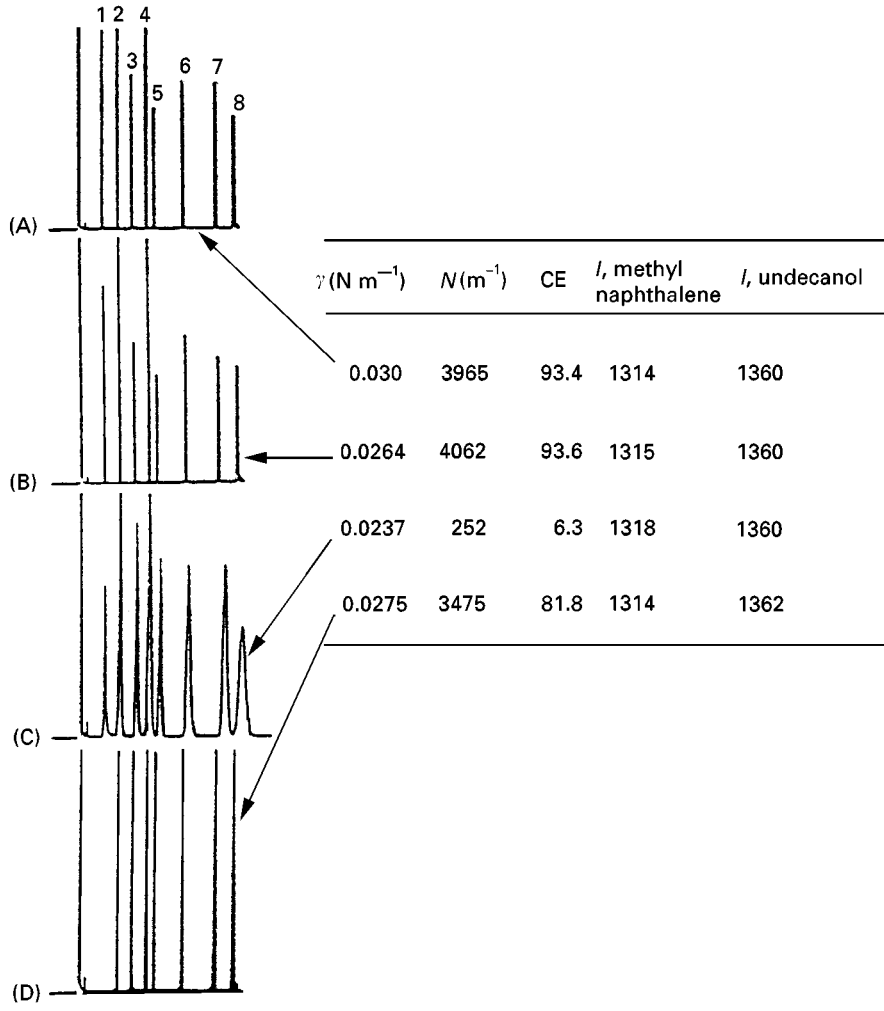


Figure 3 Chromatograms of a column test mixture on 30 m × 0.25 mm, d_f 0.25 μm columns. Test mixtures were run at 130°C isothermal, and columns ramped to higher temperatures to determine bleed profiles. Note that the 'delta bleed' is 2.32 pA at 320°C for the 'second generation' column, versus 14.42 pA for the 'conventional' column. This is essentially the 'maximum temperature' of the latter column, which has reached a point where bleed increases exponentially with temperature. The latter column is capable of still higher temperatures, however, and exhibits a bleed signal of 5.47 pA at 340°C. Key: - - -, first generation 35% diphenylpolysiloxane column; ——, second generation 35% phenyl low-bleed column.

suggests that activity sometimes depends on whether solutes 'see' the surface. As solute molecules migrate through the stationary phase toward the siliceous surface, the carrier flow sweeps the solute molecules in the gas phase downstream. To re-establish the distribution constant in that portion of the column, solute molecules in the stationary phase reverse direction and migrate toward the mobile phase. Whether this impetus to change the direction of migration occurs before or after the solute has reached the surface would, under a given set of conditions, depend on the thickness of the stationary phase film.

The affinity of the surface for polar stationary phases is sometimes estimated by measuring the surface energy of the prepared surface. While both the nature and strength of surface-to-polymer interactions are important to column performance, they are not necessarily predictable. A given 'high energy' surface is not always suitable for the deposition of a 'high energy' polymer. Architectural 'tailoring' of the surface can be as difficult as tailoring stationary-phase selectivity. The concept of 'coating efficiency', used in **Figure 4**, ($CE = 100 \times H_{theor\ min}]/\ [H_{observed}]$) is often used to measure the compatibility of a surface for a given stationary phase.

Figure 4 shows four dimensionally identical columns under the same operational conditions and coated with the same experimental high phenyl stationary phase; each column received a different deactivation treatment. Note the third example (C),



γ (N m^{-1})	N(m^{-1})	CE	I, methyl naphthalene	I, undecanol
0.030	3965	93.4	1314	1360
0.0264	4062	93.6	1315	1360
0.0237	252	6.3	1318	1360
0.0275	3475	81.8	1314	1362

Figure 4 Chromatograms of a test mixture on four dimensionally identical columns, all coated with the same experimental high phenyl stationary phase, but subjected to different deactivation pretreatments. Note the disappearance of 2-ethylhexanoic acid in (D) and the intercolumn variations in retention indices (I) for methylnaphthalene and undecanol. See text for discussion of the effects of the surface energies (γ) on coating efficiencies (CE). Solutes in order of elution: 1, 2-ethylhexanoic acid (totally adsorbed in chromatogram D); 2, 1,6-hexanediol; 3, 4-chlorophenol; 4, tridecane; 5, 2-methylnaphthalene; 6, 1-undecanol; 7, tetradecane; and 8, dicyclohexylamine.

which has high surface energy but very poor coating efficiency. (A), (B) and (D) all are nonbeaded surfaces, but the coating efficiencies of (A) and (B) are significantly better than that of (D). The coating efficiencies of these three columns vary in the order $2 > 1 > 4$, while the surface energies vary in the order $1 > 4 > 2$. The column with the lowest surface energy of the coatable surfaces (column B), yields the highest coating efficiency. In column (D), the acid peak disappeared. In every case, there is almost surely at least a slight effect on selectivity. One of our better ways for estimating this quality is the duplicability of retention indices for polar and apolar compounds, and column-to-column variations in these comparisons imply that closely eluting solutes of different functionalities may exhibit a given elution order on the one column, and a different elution order on the other column. These data indicate that both the stationary phase (which may be proprietary) and column pretreatments (which are almost always proprietary and vary from manufacturer to manufacturer) affect retention factors, separation factors, and even the elution order. Surface pretreatments, including but not limited to deactivation, can, and often do, exert profound effects on overall column performance.

Conclusions

During its half century history, gas chromatography (GC) has evolved to become the world's most widely used analytical technique. The growth has accelerated with the commercial availability of columns, the quality of which has shown consistent improvements, and by the continuing development of compatible instrumentation and combined techniques (e.g. gas chromatography–spectrometry, GC-AED, etc.). Also important to that growth is the fact that the technique possesses separation powers so great that the unskilled analyst can abuse the technique and still generate useful data. Other analytical methods (e.g. capillary electrophoresis, capillary zone electrophoresis, liquid chromatography) have shown promise of greatly increased growth, but GC has not stagnated. Many of the elements necessary for 'fast' GC have been known for some time, but their application usually requires instrumental modification and adaptation beyond the purview of most practising analysts. Some cracks in this barrier have recently appeared. Developments in more selective stationary phases, electronic pneumatic controls, micropacked columns, and shorter columns of smaller diameter now permit some users to demonstrate improved separations while reducing analysis times. Appreciable time savings have been demonstrated merely through refinement of operational parameters (temperature, program rates, gas velocity). By changing both operational and design parameters (e.g. column dimensions), analysis times using unmodified instrumentation have been reduced from 30 min to a few seconds. A greater utilization of these newer developments, however, will require honing the skills of the average analyst through continuing education.

See Colour Plates 19, 20.

See also: **II/Chromatography: Gas:** Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors); Detectors: Mass Spectrometry; Detectors: Selective; Gas-Solid Gas Chromatography; Historical Development; Sampling Systems; Theory of Gas Chromatography. **Appendix 2: Essential Guides to Method Development in Gas Chromatography.**

Further Reading

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Glossary

Based on the most recent recommendations of the International Union of Pure and Applied Chemistry (IUPAC), which appeared in *Pure and Applied Chemistry* 65: 819–872 (1993).

A Eddy diffusion, or packing factor term of the van Deemter (packed column) equation.

α Separation factor; the adjusted retention time of the more retained solute relative to that of the less retained solute.

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B Longitudinal diffusion term of the van Deemter and Golay equations.

β Column phase ratio. The column volume occupied by mobile (gas) phase relative to the volume occupied by stationary phase. In open-tubular columns: $\beta = [r_c - 2d_f]/[2d_f] \cong r_c/2d_f$.

c_M, c_S Solute concentrations in mobile and stationary phases, respectively.

C Resistance to mass transfer (or mass transfer) in the van Deemter (or Golay) equations; C_M and C_S denote mass transfer from mobile to stationary and from stationary to mobile phases, respectively.

d_c Inner diameter of the column. Both mm and μm are commonly used. The latter, while consistent with the units used for d_f, implies three significant figures, which is rarely true.

d_f Thickness of the stationary phase film, usually in μm.

D Diffusivity; D_M and D_S denote solute diffusivities in the mobile and stationary phases, respectively; usually given in $cm^2\ s^{-1}$.

F Volumetric flow of the mobile phase, usually in $cm^3\ min^{-1}$. Many practical chromatographers assume equivalency with (and hence employ) $mL\ min^{-1}$.

FID Flame ionization detector.

GC-MS The combination of gas chromatography and mass spectrometry, usually a single integrated unit in which fractions separated by GC are sequentially introduced to the MS.

H Length equivalent to one theoretical plate (height equivalent to a theoretical plate): $H = L/N$. When measured at u_{opt}, the result is termed H_{min}.

k Solute retention factor (formerly partition ratio). Ratio of the amounts of a solute (or time spent) in stationary and mobile phases, respectively. Because all solutes spend t_M time in the mobile phase, $k = [t_R - t_M]/t_M$, and $k = t'_R/t_M$.

K_c Distribution constant. Formerly K_D. Ratio of solute concentrations in stationary and mobile phases, respectively: $K_c = c_S/c_M$.

L Length of the column, usually expressed in metres for column length, in cm for the determination of $\bar{u}$, and in mm for the determination of H.

N Theoretical plate number; $N = [t_R/\sigma]^2$, where σ is the standard deviation of the peak.

N_{req} Number of theoretical plates required to separate two solutes of a given alpha and given retention factors to a given degree of resolution: $N_{req} = 16R_s^2[(k+1)/k]^2[\alpha/(\alpha-1)]^2$.

o.d. Outer diameter of the column.

r_c Inside radius of the column.

R_s Peak resolution. A measure of separation as evidenced by both the distance between the peak maxima and by the peak widths. ASTM and IUPAC definitions are based on w_b (peak width at base) measurements, which require extrapolation. If peaks are assumed to be Gaussian, then $R_s = 1.18[t_{R(B)} - t_{R(A)}]/[w_{h(A)} + w_{h(B)}]$.

σ Standard deviation of a Gaussian peak.

t_M Gas hold-up time. The time (or distance) required for a nonretained substance (e.g. mobile phase) to transit the column.

t_R Retention time. The time (or distance) from the point of injection to the peak maximum.

t'_R Adjusted retention time. Equivalent to the residence time in stationary phase; difference of the solute retention time and the gas hold-up time: $t'_R = t_R - t_M$.

$\bar{u}$ Average linear velocity of the mobile (gas) phase: $\bar{u}\ (cm\ s^{-1}) = L\ (cm)/t\ (s)$.

V Volume. V_M and V_S represent volumes of the mobile and stationary phases, respectively.

w_b Peak width at base. Determined by measuring the length of baseline defined by intercepts extrapolated from the points of inflection of the peak, and equivalent to four standard deviations in a Gaussian peak.

w_h Peak width at half-height. Measured across the peak halfway between baseline and peak maximum, this can be measured directly without extrapolation, and is equal to 2.35 standard deviations in a Gaussian peak.

Derivatization

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Introduction

Gas chromatography (GC), the longest established instrumental chromatographic technique, dominated the separation field from the early 1950s until the mid-1970s when high performance liquid chromatography (HPLC) became a competitive technique. During this 20-year period, considerable effort was expended in developing procedures to make compounds sufficiently volatile, more thermally stable and less polar so that they would be more amenable to GC analysis. Such efforts were aimed almost